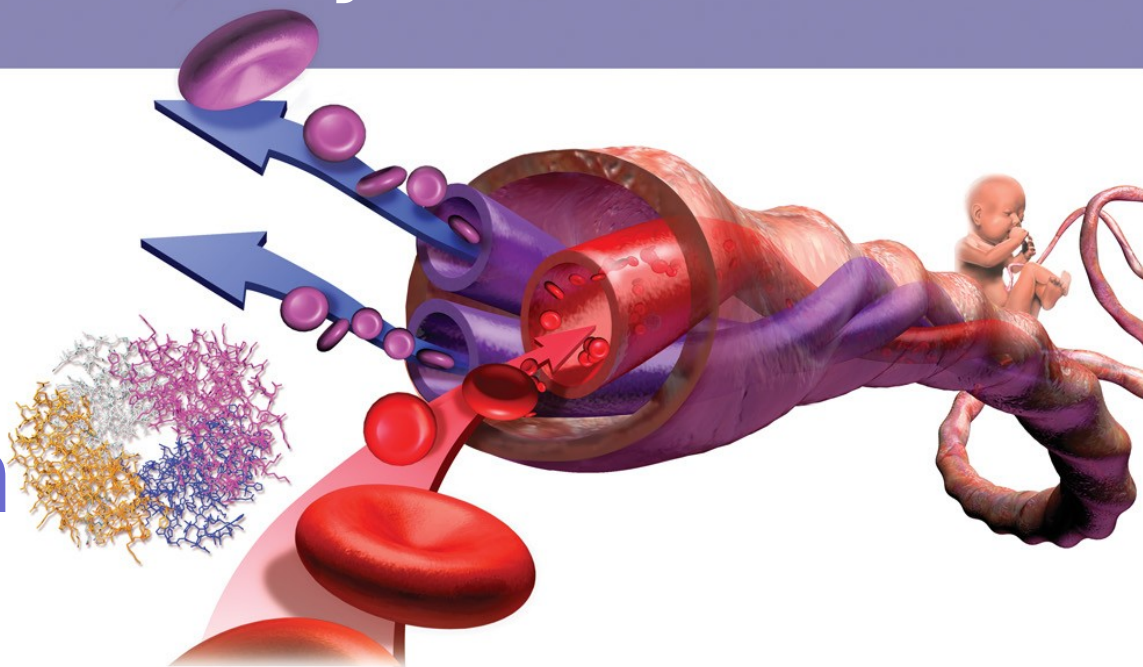


John E. McMurry - Robert C. Fay

General Chemistry: Atoms First

Chapter 13 Chemical Equilibrium



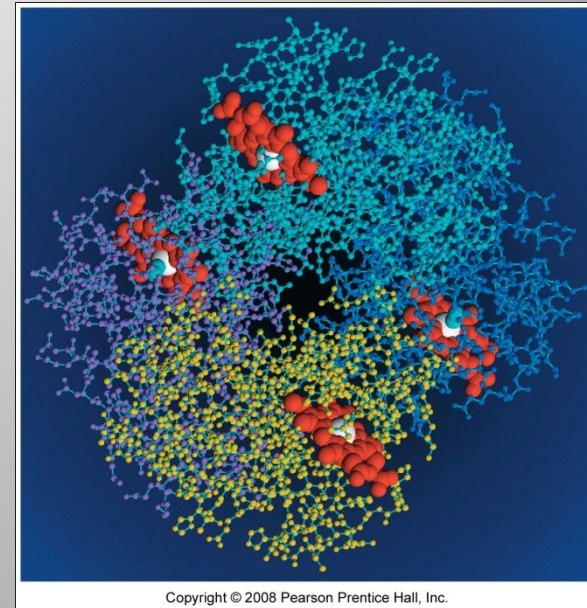
Prentice Hall

Hemoglobin

- Hemoglobin is a protein (Hb)
 - found in red blood cells
 - reacts with O₂
 - enhances amount of O₂ carried through the blood stream



- the \rightleftharpoons represents that the reaction is in **dynamic equilibrium**



Hemoglobin Equilibrium System

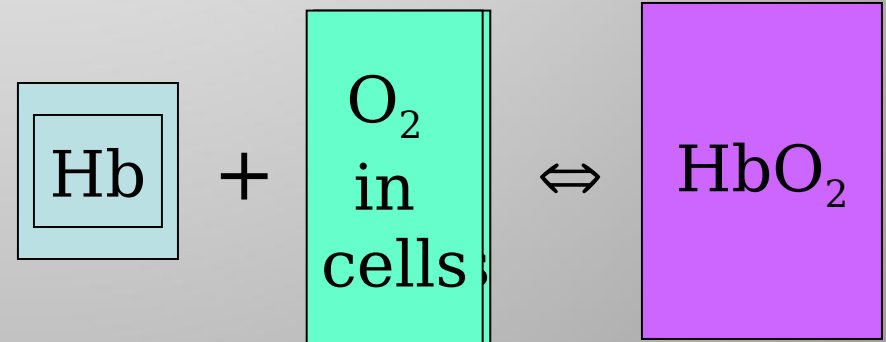


- the concentrations of Hb, O₂, and HbO₂ are all interdependent
- the relative amounts of Hb, O₂, and HbO₂ at equilibrium are related to a constant called the **equilibrium constant, *K***
 - a larger *K*, means more product exists at equilibrium
- changing concentration of any component results in the others changing to re-establish equilibrium

O₂ Transport

high [O₂] in lungs,
equilibrium shifts to
make more HbO₂

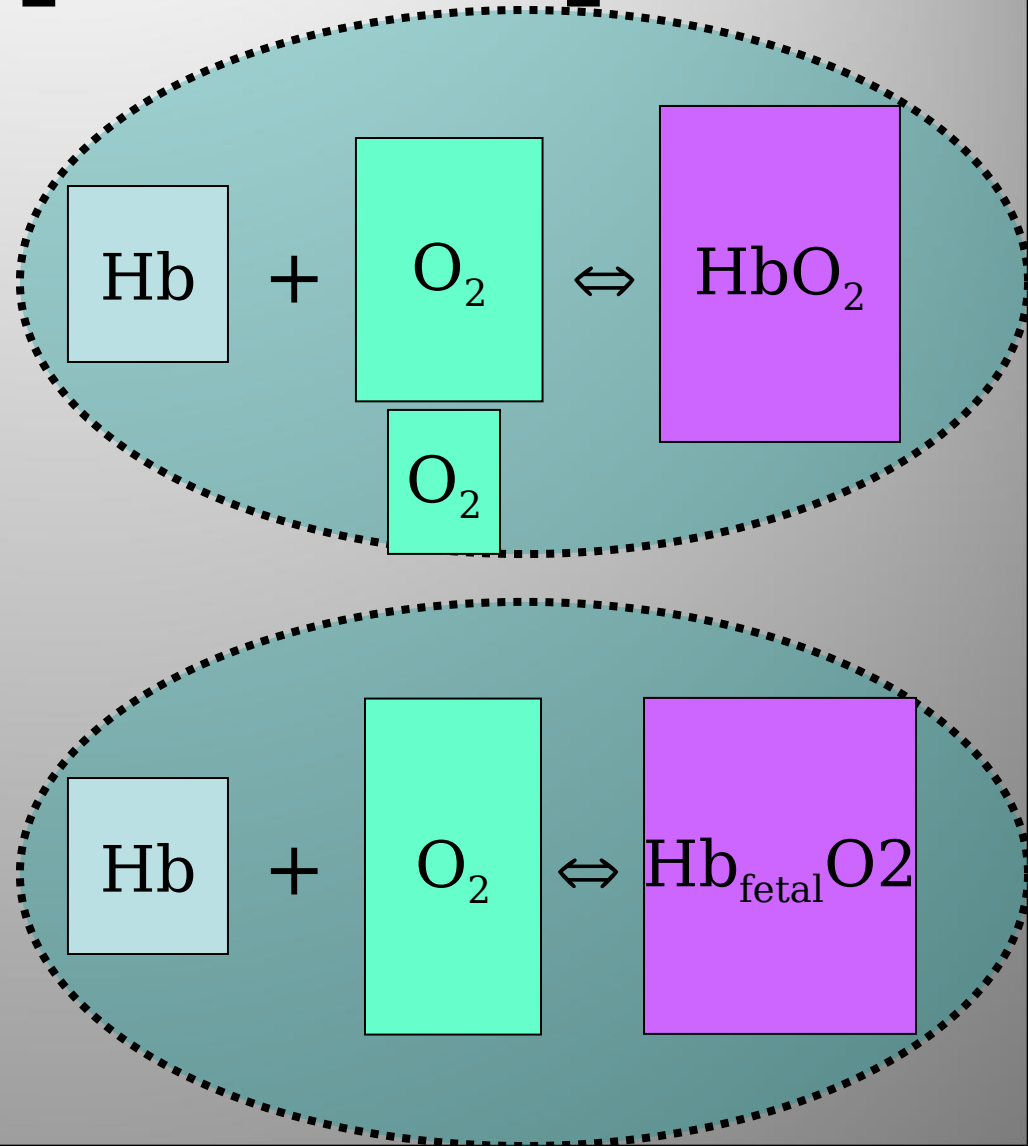
low concentration
of [O₂] in cells,
equilibrium shifts
to break down
HbO₂ and increase
the amount of free
O₂



Fetal Hemoglobin, HbF



- the equilibrium constant for fetal hemoglobin is larger than that of adult hemoglobin
- fetal hemoglobin more efficiently binds O_2 , so O_2 is transferred from the mother's hemoglobin to the fetal hemoglobin in the placenta



Reaction Dynamics

- at the start, reactants are consumed and products are made
 - forward reaction dominates (reactants \rightarrow products)
 - as reactant concentration decreases, the forward reaction rate decreases
- eventually, products can react to reform reactants
 - reverse reaction occurs (products \rightarrow reactants)
 - assumes a closed system (no escape)
 - as [product] increases, the reverse reaction rate increases
- processes that proceed in both the forward and reverse direction are said to be **reversible**
reactants \rightleftharpoons products

Hypothetical Reaction: $2 A \rightleftharpoons B$

Time

	[A]	[B]
0	0.400	0.000
10	0.208	0.096
20	0.190	0.105
30	0.180	0.110
40	0.174	0.113
50	0.170	0.115
60	0.168	0.116
70	0.167	0.117
80	0.166	0.117
90	0.165	0.118
100	0.165	0.118
110	0.164	0.118
120	0.164	0.118
130	0.164	0.118
140	0.164	0.118
150	0.164	0.118

The reaction slows over time,

But the Red molecules never run out!

At time > 90 seconds, the concentrations of both A and B molecules, no longer change - equilibrium has been

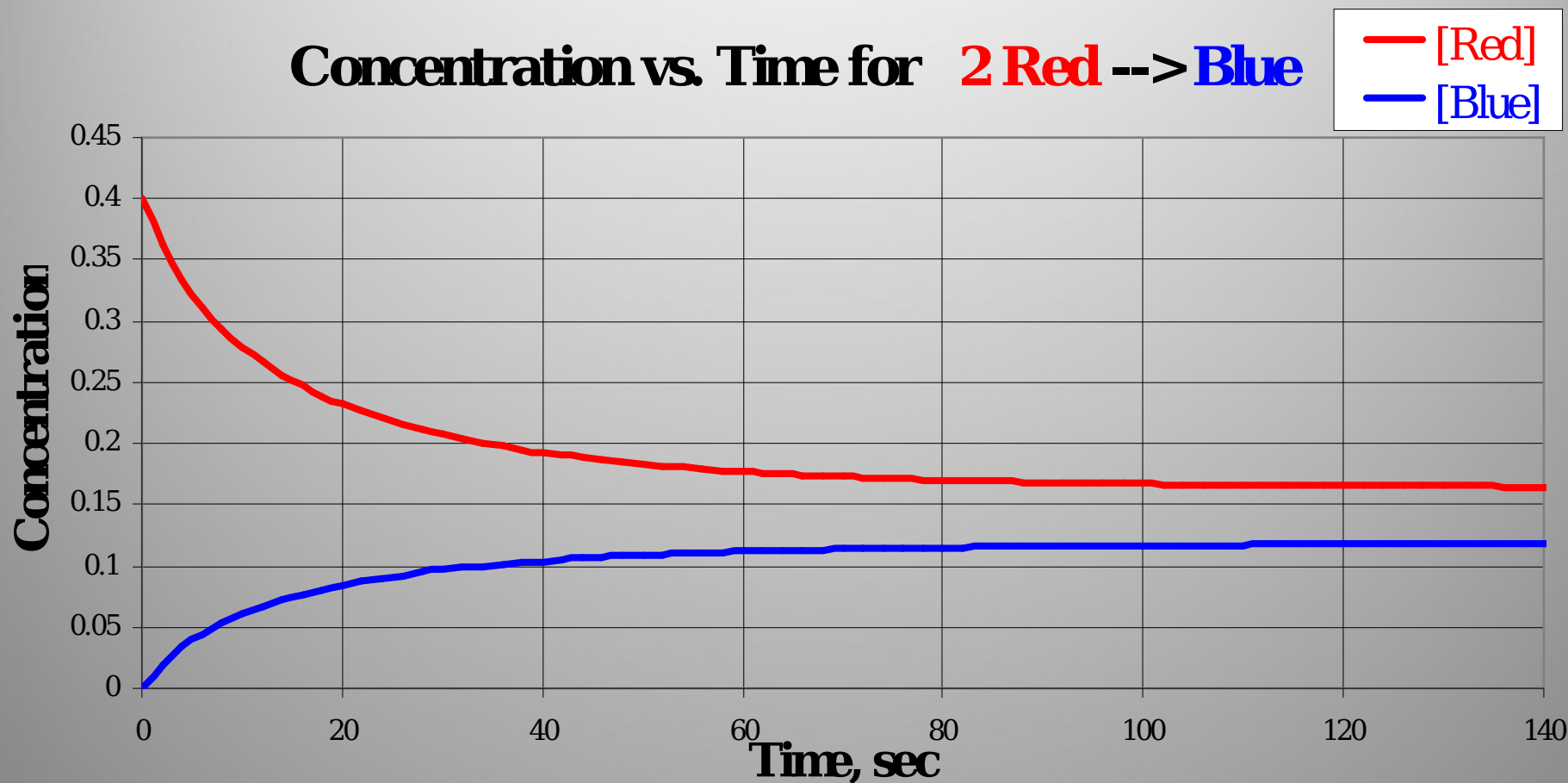
**established.
equilibrium does not mean
that the concentrations of
A and B are equal!**

Once equilibrium is established, the rate of A turning into B is the same as the rate of B molecules turning into A

Hypothetical Reaction



Concentration vs. Time for $2 \text{ Red} \rightarrow \text{Blue}$



Reaction Dynamics

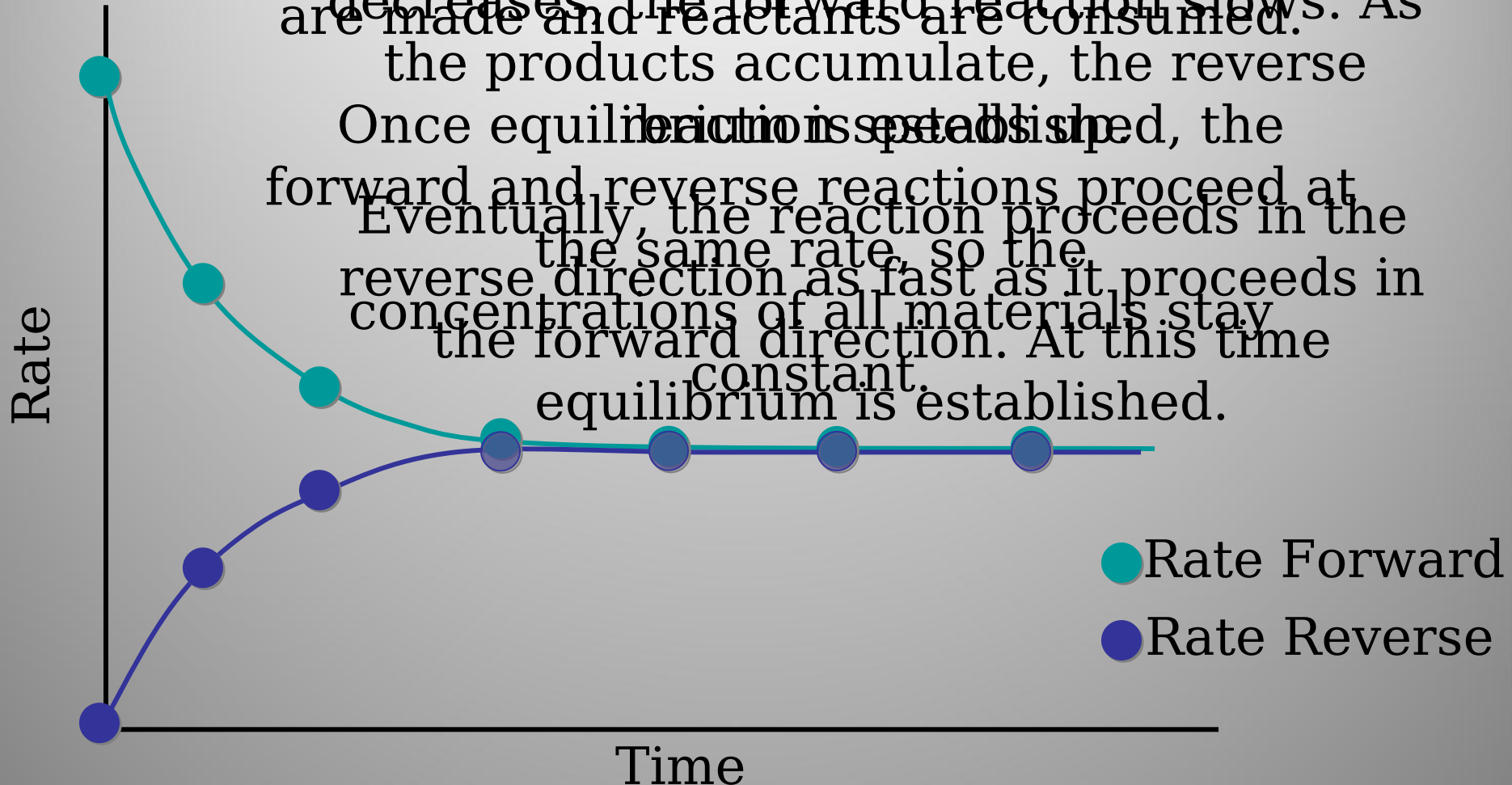
Initially, only the forward reaction takes place. Because the reactant concentration decreases, the forward reaction slows. As the forward reaction proceeds, products are made and reactants are consumed.

As the products accumulate, the reverse

reaction is established.

Once equilibrium is established, the forward and reverse reactions proceed at

Eventually, the reaction proceeds in the reverse direction as fast as it proceeds in the forward direction. At this time equilibrium is established.

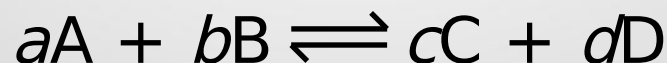


Equilibrium \neq Equal

- some reactions reach equilibrium only after almost all the reactant molecules are consumed
 - the position of equilibrium favors the products
- other reactions reach equilibrium when only a small percentage of the reactant molecules are consumed
 - the position of equilibrium favors the reactants
- Equilibrium **does not mean** that the $[\text{reactants}] = [\text{products}]$.

The Equilibrium Constant

For a general reversible reaction:



The Equilibrium Equation is:

Equilibrium constant \nearrow $K_{eq} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$

\leftarrow Products

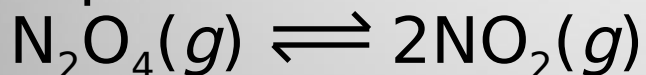
\leftarrow Reactants

Equilibrium constant expression

Remember good **PR**,
Products come first on the top,
Reactants go on the bottom

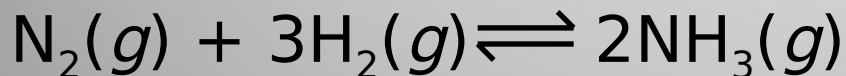
The Equilibrium Constant

The equilibrium constant K_c and the equilibrium constant expression are for the chemical equation *as written*.



$$K_{\text{eq}} = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]}$$

$$= 4.64 \times 10^{-3} \text{ (at } 25^\circ\text{C)}$$



$$K_{\text{eq}} = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$$

$$2\text{NH}_3(g) \rightleftharpoons \text{N}_2(g) + 3\text{H}_2(g) \quad K_{\text{eq (reverse)}} = \frac{[\text{N}_2][\text{H}_2]^3}{[\text{NH}_3]^2} = \frac{1}{K_{\text{eq}}}$$

$$2\text{N}_2(g) + 6\text{H}_2(g) \rightleftharpoons 4\text{NH}_3(g) \quad K_{\text{eq (doubled)}} = \frac{[\text{NH}_3]^4}{[\text{N}_2]^2[\text{H}_2]^6} = K_{\text{eq}}^2$$

Equilibrium Constant

- the relationship between the chemical equation and the concentrations of reactants and products is called the **Law of Mass Action**
- **K** , the **equilibrium constant**
 - Is unit-less
 - Is always written as products over reactants

What Does the Value of K_{eq} Imply?

- when $K_{eq} \gg 1$, at equilibrium product molecules predominate
 - the position of equilibrium favors products
- when $K_{eq} \ll 1$, at equilibrium reactant molecules predominate
 - the position of equilibrium favors reactants

Relationships between K and Chemical Equations

For $K_{\text{backwards}}$, the equilibrium constant is inverted

for the reaction $aA + bB \rightleftharpoons cC + dD$

the equilibrium constant expression is:

$$K_{\text{eq (forward)}} = \frac{[C]^c \times [D]^d}{[A]^a \times [B]^b}$$

for the reverse reaction

$cC + dD \rightleftharpoons aA + bB$

the equilibrium

expression is:

$$K_{\text{eq (backward)}} = \frac{[A]^a \times [B]^b}{[C]^c \times [D]^d}$$

$$K_{\text{eq (forward)}} = \frac{1}{K_{\text{eq (backward)}}}$$

Relationships between K and Chemical Equations

When an equations coefficients are multiplied by a factor, the equilibrium constant is raised to that factor

for the reaction $aA + bB \rightleftharpoons cC$

the equilibrium constant expression is:

$$K_{\text{original}} = \frac{[C]^c}{[A]^a \times [B]^b}$$

$$K_{\text{new}} = K_{\text{original}}$$

for the reaction $2aA + 2bB \rightleftharpoons 2cC$

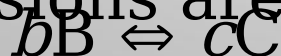
the equilibrium constant expression is:

$$K_{\text{new}} = \frac{[C]^{2c}}{[A]^{2a} \times [B]^{2b}} = \left(\frac{[C]^c}{[A]^a \times [B]^b} \right)^2$$

Relationships between K and Chemical Equations

- when you add equations to get a new equation, the equilibrium constant of the new equation is the product of the equilibrium constants of the old equations

For reactions (1) and (2) below, the equilibrium constant expressions are:



$$K_1 = \frac{[B]^b}{[A]^a}$$

$$K_2 = \frac{[C]^c}{[B]^b}$$

$$K_{\text{new}} = K_1 \times K_2$$

for the reaction $aA \rightleftharpoons cC$

the equilibrium constant expression is:

$$K_{\text{new}} = \frac{[C]^c}{[A]^a}$$

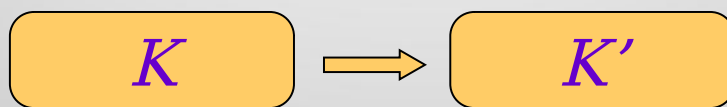
$$= \frac{[B]^b}{[A]^a} \times \frac{[C]^c}{[B]^b}$$

Compute the equilibrium constant at 25°C for the reaction $\text{NH}_3(g) \rightleftharpoons 0.5 \text{N}_2(g)$

Given: for $\text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g)$, $K = 3.7 \times 10^8$ at 25°C

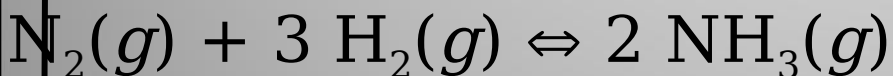
Find: K for $\text{NH}_3(g) \rightleftharpoons 0.5\text{N}_2(g) + 1.5\text{H}_2(g)$, at 25°C

Concept Plan:

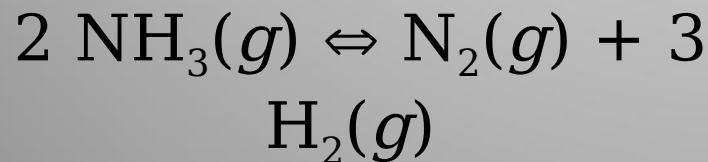


$$K_{\text{backward}} = 1/K_{\text{forward}}, K_{\text{new}} = K_{\text{old}}^n$$

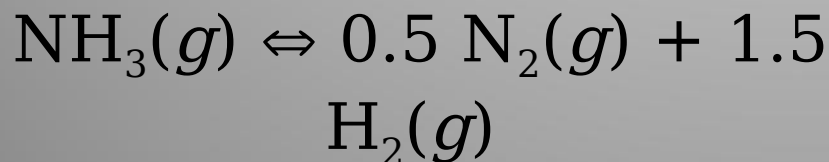
Relationship Solution:



$$K_1 = 3.7 \times 10^8$$



$$K_2 = \frac{1}{K_1} = \frac{1}{3.7 \times 10^8}$$



$$K' = (K_2)^{1/2} = \left(\frac{1}{3.7 \times 10^8} \right)^{1/2}$$

$$K' = 5.2 \times 10^{-5}$$

Equilibrium Constants for Reactions Involving Gases

- the [gas] in a mixture is proportional to its partial pressure
- therefore, the equilibrium constant can be expressed as the ratio of the partial pressures of the gases
- for $aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g)$ the equilibrium constant expressions are

$$K_c = \frac{[C]^c \times [D]^d}{[A]^a \times [B]^b} \longrightarrow K_p = \frac{P_C^c \times P_D^d}{P_A^a \times P_B^b}$$

K_c and K_p

- in calculating K_p , the partial pressures are always in **atm**
- the values of K_p and K_c are not necessarily the same because of the difference in units

The Equilibrium Constant

$$K_p = K_c (RT)^{\Delta n}$$

R is the gas constant $0.082058 \frac{\text{L atm}}{\text{mol K}}$

T is the absolute temperature (Kelvin).

Δn is the # of moles of gaseous products minus the # of moles of gaseous reactants.

✓ $K_p = K_{eq}$ when $\Delta n = 0$

Deriving the Relationship between K_p and K_{eq}

$$[A] = \frac{n_A}{V} \quad \left(\frac{\text{moles of A}}{\text{volume of gas}} \right)$$

$$P_A V = n_A RT, \text{ from the Ideal Gas Law}$$

$$P_A = \frac{n_A}{V} RT = [A] RT \quad (\text{substituting } [A] \text{ for } \frac{n_A}{V})$$

$$\therefore [A] = \frac{P_A}{RT}$$

Deriving the Relationship Between K_p and K_c

for $aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g)$

$$K_c = \frac{[C]^c \times [D]^d}{[A]^a \times [B]^b}$$

$$[X] = \frac{P_X}{RT}$$

$$K_p = \frac{P_C^c \times P_D^d}{P_A^a \times P_B^b}$$

substituting

$$K_c = \frac{\left(\frac{P_C}{RT}\right)^c \times \left(\frac{P_D}{RT}\right)^d}{\left(\frac{P_A}{RT}\right)^a \times \left(\frac{P_B}{RT}\right)^b} = \frac{P_C^c P_D^d \left(\frac{1}{RT}\right)^{c+d}}{P_A^a P_B^b \left(\frac{1}{RT}\right)^{a+b}} = K_p \left(\frac{1}{RT}\right)^{(c+d)-(a+b)}$$

$$\text{rearranging} \quad K_p = K_c (RT)^{(c+d)-(a+b)} = K_c (RT)^{\Delta n}$$

Find K_c for the reaction $2 \text{NO}(g) + \text{O}_2(g) \rightleftharpoons 2 \text{NO}_2(g)$, given $K_p = 2.2 \times 10^{12}$ @ 25°C

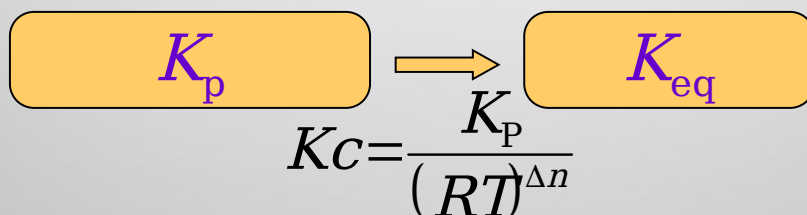
Given:

$$K_p = 2.2 \times 10^{12}$$

Find:

$$K_c$$

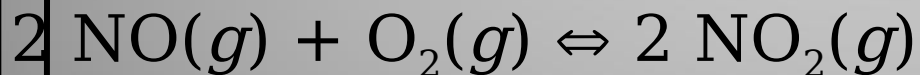
Concept Plan:



Relationships :

$$K_p = K_c (RT)^{\Delta n}$$

Solution:



$$\Delta n = 2 - 3 = -1$$

$$K_c = \frac{K_p}{(RT)^{\Delta n}} = \frac{2.2 \times 10^{12}}{\left(0.08206 \frac{\text{atm}\cdot\text{L}}{\text{mol}\cdot\text{K}} \times 298\text{K}\right)^{-1}} = 5.4 \times 10^{13}$$

Check:

K is a unitless number
since there are more moles of reactant than product, K_{eq} should be larger than K_p , and it is

Heterogeneous Equilibria

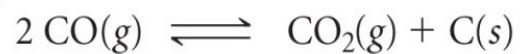
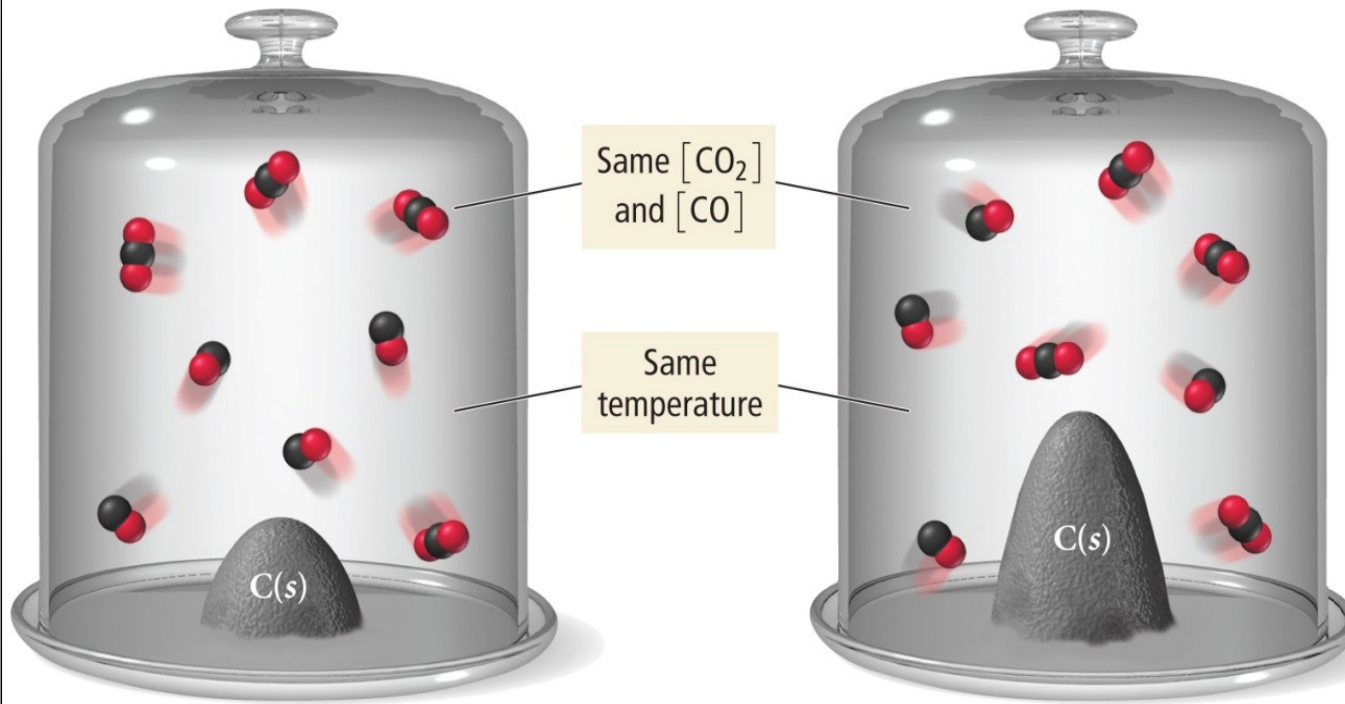
- pure solids and pure liquids are materials whose concentration doesn't change during the course of a reaction
 - its amount can change, but the amount of it in solution doesn't because it really isn't in solution
- because their concentration doesn't change, solids and liquids are not included in the equilibrium constant expression
 - If a subscript (l) or (s) appears, don't include them in the expression
- for the reaction $aA_{(s)} + bB_{(aq)} \rightleftharpoons cC_{(l)} + dD_{(aq)}$ the equilibrium constant expression is:

$$K_c = \frac{[D]^d}{[B]^b}$$

Heterogeneous Equilibria

The amount of C is different, but the amounts of CO and CO₂ remains the same. Therefore the amount of C has no effect on the position of

A Heterogeneous Equilibrium.



$$K_c = \frac{[\text{CO}_2]}{[\text{CO}]^2}$$
$$K_p = \frac{P_{\text{CO}_2}}{P_{\text{CO}}^2}$$

Calculating Equilibrium Constants from Measured Equilibrium Concentrations

- the most direct way to find the equilibrium constant is to measure the amounts of reactants and products in a mixture at equilibrium
 - measure one amount
 - use stoichiometry to calculate the other amounts
- the equilibrium mixture may have different amounts of reactants and products, but the value of the equilibrium constant will always be the same
 - at constant temperature
 - the equilibrium constant is independent of the initial amounts of reactants and products

Initial and Equilibrium Concentrations for $\text{H}_2(g) + \text{I}_2(g)$

Initial			Equilibrium			Equilibrium Constant
$[\text{H}_2]$	$[\text{I}_2]$	$[\text{HI}]$	$[\text{H}_2]$	$[\text{I}_2]$	$[\text{HI}]$	$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$
0.50	0.50	0.0	0.11	0.11	0.78	$\frac{[0.78]^2}{[0.11][0.11]} = 50$
0.0	0.0	0.50	0.055	0.055	0.39	$\frac{[0.39]^2}{[0.055][0.055]} = 50$
0.50	0.50	0.50	0.165	0.165	1.17	$\frac{[1.17]^2}{[0.165][0.165]} = 50$

Calculating Equilibrium Concentrations

- Stoichiometry can be used to determine the equilibrium concentrations of all reactants and products if you know initial concentrations and one equilibrium concentration
- given $2 A_{(aq)} + B_{(aq)} \rightleftharpoons 4 C_{(aq)}$ with initial concentrations $[A] = 1.00 \text{ M}$, $[B] = 1.00 \text{ M}$, and $[C] = 0$. You then measure the equilibrium concentration of C as $[C] = 0.50 \text{ M}$.

	[A]	[B]	[C]
initial molarity	1.00	1.00	0
change in concentration	$-1/2(0.50)$	$1/4(0.50)$	$+0.50$
equilibrium molarity	0.75	0.88	0.50

Find the value of K_c for the reaction
 $2 \text{CH}_4(g) \rightleftharpoons \text{C}_2\text{H}_2(g) + 3 \text{H}_2(g)$ at
 1700°C if the initial $[\text{CH}_4] = 0.115 \text{ M}$
and the equilibrium $[\text{C}_2\text{H}_2] = 0.035 \text{ M}$

Construct an
ICE table for the
reaction

for the
substance whose
equilibrium
concentration is
known, calculate
the change in
concentration

	$[\text{CH}_4]$	$[\text{C}_2\text{H}_2]$	$[\text{H}_2]$
initial	0.115	0.000	0.000
change			
equilibrium		0.035	

Find the value of K_c for the reaction
 $2 \text{CH}_4(g) \rightleftharpoons \text{C}_2\text{H}_2(g) + 3 \text{H}_2(g)$ at
 1700°C if the initial $[\text{CH}_4] = 0.115 \text{ M}$
and the equilibrium $[\text{C}_2\text{H}_2] = 0.035 \text{ M}$

use the known
change to
determine the
change in the
other materials

add the change
to the initial
concentration to
get the
equilibrium
concentration in
each column

use the

	$[\text{CH}_4]$	$[\text{C}_2\text{H}_2]$	$[\text{H}_2]$
initial	0.115	0.000	0.000
change	-0.045	+0.035	+0.105
equilibrium	0.070	0.035	0.105

$$K_c = \frac{[\text{C}_2\text{H}_2][\text{H}_2]^3}{[\text{CH}_4]^2}$$

$$= \frac{(0.035)(0.105)^3}{(0.045)^2} = 0.020$$

*****The following data were collected for the reaction: $2 \text{NO}_2(g) \rightleftharpoons \text{N}_2\text{O}_4(g)$ at 100°C . Complete the table and determine values of K_p and K_c for each**

experiment.	Expt 1	Expt 2
initial $[\text{N}_2\text{O}_4]$	0	0.0200
initial $[\text{NO}_2]$	0.0200	0
change $[\text{N}_2\text{O}_4]$	-0.00140	-0.0155*
change $[\text{NO}_2]$	-0.00280	+0.0310
equilibrium $[\text{N}_2\text{O}_4]$	0.00140	0.00452
equilibrium $[\text{NO}_2]$	0.0172	0.0310

***rounded off**

The following data were collected for the reaction: $2 \text{NO}_2(g) \rightleftharpoons \text{N}_2\text{O}_4(g)$ at 100°C . Complete the table and determine values of K_p and K_c for each experiment.

- $K_c = [\text{N}_2\text{O}_4]/[\text{NO}_2]^2$

- For exp. 1:

$$K_c = [\text{N}_2\text{O}_4]/[\text{NO}_2]^2 = .00140/.0172^2 = 4.73$$

- For exp. 2:

$$K_c = [\text{N}_2\text{O}_4]/[\text{NO}_2]^2 = .00452/.0310^2 = 4.70$$

The Reaction Quotient

- if a reaction mixture, is not at equilibrium; you can determine the direction the reaction will proceed
 - by comparing the current concentration ratios to the equilibrium constant
- the non-equilibrium ratio of the [products] and the [reactants] (raised to the power of their coefficients) is called the **reaction quotient, Q**

for the gas phase reaction



the reaction quotient

$$Q_c = \frac{[C]^c \times [D]^d}{[A]^a \times [B]^b}$$

$$Q_p = \frac{P_C^c \times P_D^d}{P_A^a \times P_B^b}$$

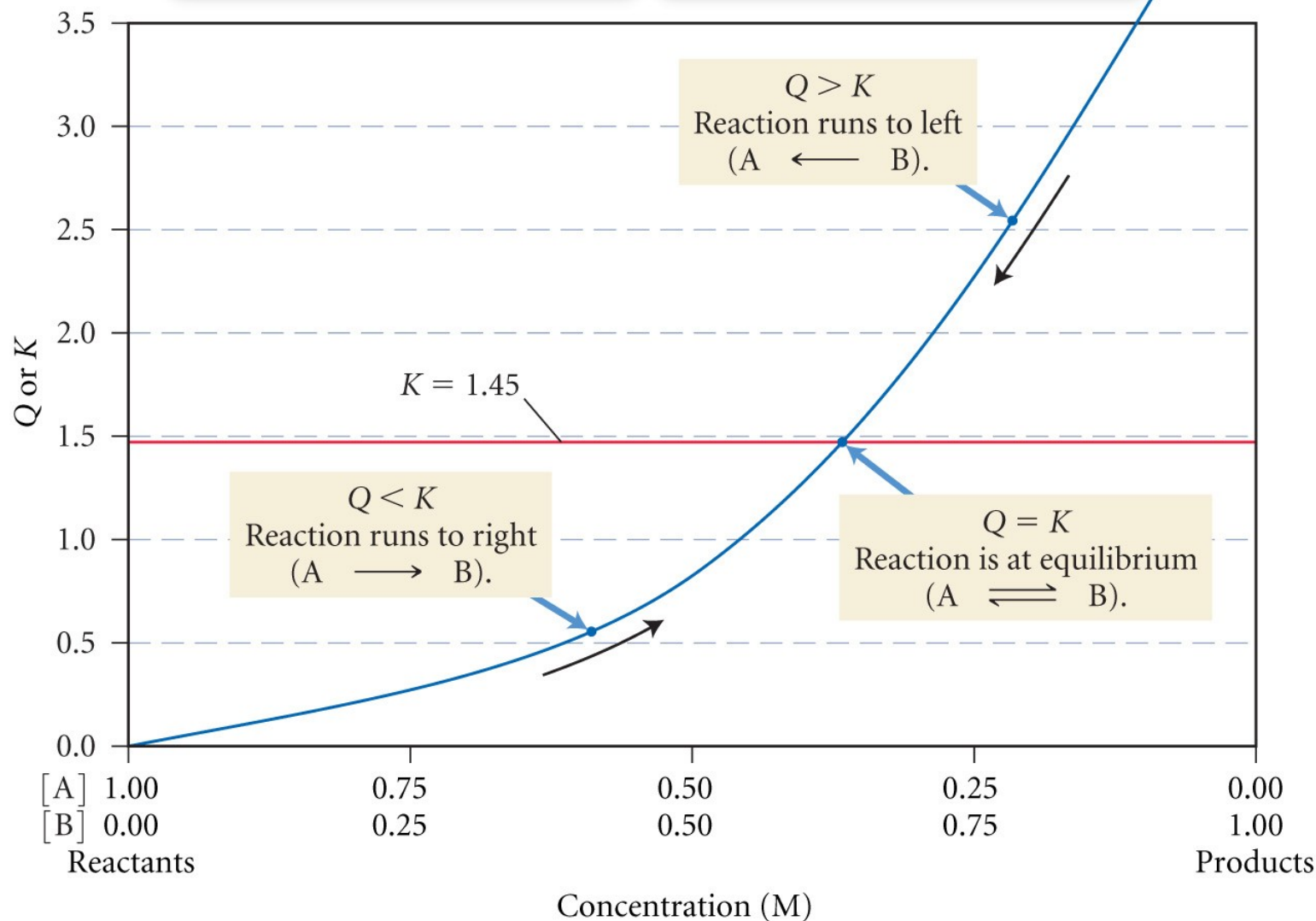
The Reaction Quotient: Predicting the Direction of Change

- if $Q > K$, the reaction will proceed in reverse
 - the [products] will decrease and [reactants] will increase
- if $Q < K$, the reaction will proceed forward
 - the [products] will increase and [reactants] will decrease
- if $Q = K$, the reaction is at equilibrium
 - the [products] and [reactants] will not change

Q, K, and the Direction of Reaction

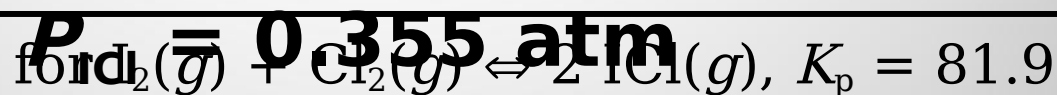
$$A(g) \rightleftharpoons B(g) \quad Q = \frac{[B]}{[A]}$$

$$Q \longrightarrow \infty \text{ at } [A] = 0, [B] = 1$$



For the reaction below, which direction will it proceed if $P_{I_2} = 0.114 \text{ atm}$, $P_{Cl_2} = 0.102 \text{ atm}$ & $P_{ICl} = 0.355 \text{ atm}$

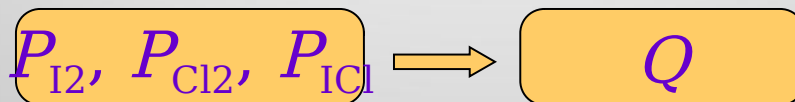
Given:



Find:

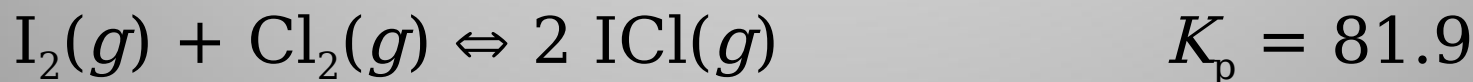
direction reaction will proceed

Concept Plan:



Relationship Solution:

If $Q = K$, equilibrium; If $Q < K$, forward; If $Q > K$, reverse



$$Q_p = \frac{P_{ICl}^2}{P_{I_2} \cdot P_{Cl_2}} = \frac{(0.355)^2}{(0.114)(0.102)}$$

$$Q_p = 10.8$$

Since $Q_p (10.8) < K_p (81.9)$, the reaction will proceed to the right

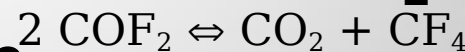
If $[\text{COF}_2]_{\text{eq}} = 0.255 \text{ M}$ and $[\text{CF}_4]_{\text{eq}} = 0.118 \text{ M}$, and $K_c = 2.00$ @ 1000°C , find the $[\text{CO}_2]_{\text{eq}}$ for

Sort: You're given the reaction and K_c . You're also given the $[X]_{eq}$ of all but one of the chemicals

Given: $\text{COF}_2(g) \rightleftharpoons \text{CO}(g) + \text{F}_2(g)$

Given:

Find:

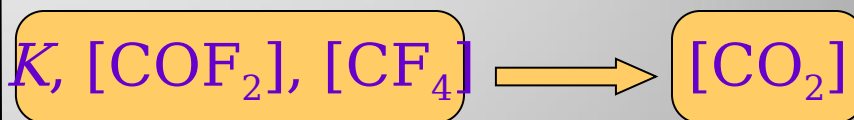


given: $[\text{COF}_2]_{\text{eq}} = 0.255 \text{ M}$, $[\text{CF}_4]_{\text{eq}} = 0.118 \text{ M}$

$$[\text{CO}_2]_{\text{eq}}$$

Strategize: You can calculate the missing concentration by using the equilibrium constant expression

Concept Plan:



Relationships:

$$K_c = \frac{[\text{CO}_2][\text{CF}_4]}{[\text{COF}_2]^2}$$

Solve: Solve the equilibrium constant expression for the unknown quantity by substituting in the given amounts

Solution:

$$K_c = \frac{[\text{CO}_2][\text{CF}_4]}{[\text{COF}_2]^2}$$

$$[\text{CO}_2] = K_{\text{c}} \cdot \frac{[\text{COF}_2]^2}{[\text{CF}_4]}$$

$$=(2.00) \frac{(0.255)^2}{(0.118)} = 1.10 \text{ M}$$

Check: Round to 1 sig fig and substitute back in

Check:

Units & Magnitude OK

PCl₅(g) is placed in a 0.500 L container and heated to 160°C. The PCl₅ decomposes into PCl₃(g) & Cl₂(g). At equilibrium, 0.203 moles of PCl₃ & Cl₂ are formed. K_c = 0.0635-Determine the equilibrium concentration of PCl₅

equilibrium concentration , M	?	$\frac{0.203 \text{ mol}}{0.500 \text{ L}}$	$\frac{0.203 \text{ mol}}{0.500 \text{ L}}$
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$$K_c = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]}$$

$$[\text{PCl}_5] = \frac{[\text{PCl}_3][\text{Cl}_2]}{K_c} = \frac{(0.406)(0.406)}{(0.0635)}$$

$$[\text{PCl}_5] = 2.60 \text{ M}$$

Finding Equilibrium Concentrations When Given the Equilibrium Constant and Initial Concentrations or Pressures

- **compare Q to K**
 - decide which direction the reaction will proceed
- **define the changes in concentration in terms of x**
 - use the coefficient from the chemical equation for the coefficient of x
 - the change is $+$ for materials on the side the reaction is proceeding toward
 - the change is $-$ for materials on the side the reaction is proceeding away from
- **solve for x**
 - for 2nd order equations, take square roots of both sides or use the quadratic formula
 - may be able to simplify and approximate answer for very large or small equilibrium constants

For the reaction $\text{I}_2(g) + \text{Cl}_2(g) \rightleftharpoons 2 \text{ICl}(g)$ @ 25°C , $K_p = 81.9$. If the initial partial pressures are all 0.100 atm, find the equilibrium concentrations

Construct an ICE table for the reaction

determine the direction the reaction is proceeding

	$[\text{I}_2]$	$[\text{Cl}_2]$	$[\text{ICl}]$
initial	0.100	0.100	0.100
change			
equilibrium			

$$Q_p = \frac{P_{\text{ICl}}^2}{P_{\text{I}_2} \cdot P_{\text{Cl}_2}} = \frac{(0.100)^2}{(0.100) \times (0.100)}$$

$$Q_p = 1$$

since $Q_p(1) < K_p(81.9)$, the reaction is proceeding forward

For the reaction $\text{I}_2(g) + \text{Cl}_2(g) \rightleftharpoons 2 \text{ICl}(g)$ @ 25°C , $K_p = 81.9$. If the initial partial pressures are all 0.100 atm, find the equilibrium concentrations

represent the change in the partial pressures in terms of x

sum the columns to find the equilibrium concentrations in terms of x

substitute into the equilibrium constant expression and solve for x

	$[\text{I}_2]$	$[\text{Cl}_2]$	$[\text{ICl}]$
initial	0.100	0.100	0.100
change	$-x$	$-x$	$+2x$
equilibrium	$0.100 - x$	$0.100 - x$	$0.100 + 2x$

$$K_p = \frac{P_{\text{ICl}}^2}{P_{\text{I}_2} \cdot P_{\text{Cl}_2}}$$

$$81.9 = \frac{(0.100 + 2x)^2}{(0.100 - x) \times (0.100 - x)} = \frac{(0.100 + 2x)^2}{(0.100 - x)^2}$$

For the reaction $\text{I}_2(g) + \text{Cl}_2(g) \rightleftharpoons 2 \text{ICl}(g)$ @ 25°C , $K_p = 81.9$. If the initial partial pressures are all 0.100 atm, find the

substitute into the equilibrium constant expression and solve for x

equilibrium concentrations

	$[\text{I}_2]$	$[\text{Cl}_2]$	$[\text{ICl}]$
initial	0.100	0.100	0.100
change	$-x$	$-x$	$+2x$
equilibrium	$0.100-x$	$0.100-x$	$0.100+2x$

$$\sqrt{81.9} = \frac{(0.100+2x)^2}{(0.100-x)^2} = \frac{(0.100+2x)}{(0.100-x)} \quad \sqrt{81.9}(0.100-x) = 0.100+2x$$

$$\sqrt{81.9}(0.100-x) = 0.100+2x$$

$$\sqrt{81.9}(0.100) - \sqrt{81.9}(x) = 0.100+2x$$

$$\sqrt{81.9}(0.100) - 0.100 = 2x + \sqrt{81.9}(x)$$

$$0.805 = 1.105x$$

$$0.0729 = x$$

For the reaction $\text{I}_2(g) + \text{Cl}_2(g) \rightleftharpoons 2 \text{ICl}(g)$ @ 25°C , $K_p = 81.9$. If the initial partial pressures are all 0.100 atm, find the

substitute x into the equilibrium concentration definition and solve

equilibrium concentrations

	$[\text{I}_2]$	$[\text{Cl}_2]$	$[\text{ICl}]$
initial	0.100	0.100	0.100
change	-0.0729	-0.0729	$2(0.0729)$
equilibrium	$0.100 - 0.0729 = 0.0271$	$0.100 - 0.0729 = 0.0271$	$0.100 + 2(0.0729) = 0.2458$

$$P_{\text{I}_2} = 0.100 - x = 0.100 - 0.0729 = 0.0271 \text{ atm}$$

$$P_{\text{Cl}_2} = 0.100 - x = 0.100 - 0.0729 = 0.0271 \text{ atm}$$

$$P_{\text{ICl}} = 0.100 + 2x = 0.100 + 2(0.0729) = 0.2458 \text{ atm}$$

For the reaction $\text{I}_2(g) + \text{Cl}_2(g) \rightleftharpoons 2 \text{ICl}(g)$ @ 25°C , $K_p = 81.9$. If the initial partial pressures are all 0.100 atm, find the

check by substituting the equilibrium concentrations back into the equilibrium constant expression and comparing the calculated K to the given K

equilibrium concentrations

	$[\text{I}_2]$	$[\text{Cl}_2]$	$[\text{ICl}]$
initial	0.100	0.100	0.100
change	-0.0729	-0.0729	2(0.0729)
equilibrium	0.027	0.027	0.246

$$K_p = \frac{P_{\text{ICl}}^2}{P_{\text{I}_2} \cdot P_{\text{Cl}_2}}$$

$$K_p = \frac{(0.246)^2}{(0.027) \times (0.027)} = 83$$

$K_p(\text{calculated}) = K_p(\text{given})$ within significant figures

For the reaction $\text{I}_2(g) \rightleftharpoons 2 \text{I}(g)$ the value of

$K_c = 3.76 \times 10^{-5}$ at 1000 K. If 1.00 moles of I_2 is placed into a 2.00 L flask and

heated, what will be the equilibrium concentrations of $[\text{I}_2]$ and $[\text{I}]$?

	$[\text{I}_2]$	$[\text{I}]$
initial	0.500	0
change	$-x$	$+2x$
equilibrium	$0.500 - x$	$2x$

(Hint: you will need to use the quadratic formula to solve for x)

since $[\text{I}]_{\text{initial}} = 0$, $Q = 0$ and the reaction must proceed forward

$$K_c = \frac{[\text{I}]^2}{[\text{I}_2]}$$

$$3.76 \times 10^{-5} = \frac{(2x)^2}{(0.500 - x)}$$

$$3.76 \times 10^{-5}(0.500 - x) = 4x^2$$

For the reaction $\text{I}_2(g) \rightleftharpoons 2 \text{I}(g)$ the value of

$K_c = 3.76 \times 10^{-5}$ at 1000 K. If 1.00 moles of I_2 is placed into a 2.00 L flask and

heated, what will be the equilibrium concentrations of I_2 and I ?

	$[\text{I}_2]$	$[\text{I}]$
initial	0.500	0
change	$-x$	$+2x$
equilibrium	$0.500 - x$	$2x$

$$K_c = \frac{[\text{I}]^2}{[\text{I}_2]} = 3.76 \times 10^{-5}$$

$$1.88 \times 10^{-5} - 3.76 \times 10^{-5} x = 4x^2$$

$$0 = 4x^2 + 3.76 \times 10^{-5} x - 1.88 \times 10^{-5}$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \quad (\text{note only one root will be reasonable})$$

$$x = \frac{-(3.76 \times 10^{-5}) \pm \sqrt{(3.76 \times 10^{-5})^2 - 4(4)(-1.88 \times 10^{-5})}}{2(4)}$$

$$x = 0.00216$$

For the reaction $\text{I}_2(g) \rightleftharpoons 2 \text{I}(g)$ the value of

$K_c = 3.76 \times 10^{-5}$ at 1000 K. If 1.00 moles of I_2 is placed into a 2.00 L flask and

heated, what will be the equilibrium

concentrations of I_2 and I ? $0.500 - 0.00216 = 0.498$

	$[\text{I}_2]$	$[\text{I}]$
initial	0.500	0
change	$-x$	$+2x$
equilibrium	0.498	0.00432

$$[\text{I}_2] = 0.498 \text{ M}$$

$$2(0.00216) = 0.00432$$

$$[\text{I}] = 0.00432 \text{ M}$$

$$\checkmark K_c = \frac{[\text{I}]^2}{[\text{I}_2]} = \frac{(0.00432)^2}{(0.498)} = 3.75 \times 10^{-5} \quad \square$$

Approximations to Simplify the Math

- when the K is very small, the position of equilibrium favors the reactants
- for relatively large initial concentrations of reactants, the reactant concentration will not change significantly when it reaches equilibrium
 - the $[X]_{\text{equilibrium}} = ([X]_{\text{initial}} - ax) \approx [X]_{\text{initial}}$
 - we are approximating the equilibrium concentration of reactant to be the same as the initial concentration
 - assuming the reaction is proceeding forward

Checking the Approximation and

Refining as Necessary

- we can check our approximation by comparing the approximate value of x to the initial concentration
- if the approximate value of x is less than 5% of the initial concentration, the approximation is valid

if $\frac{\text{approximate } x}{\text{initial concentration}} \times 100\% < 5\%$, the approximation is valid

For the reaction $2 \text{H}_2\text{S}(g) \rightleftharpoons 2 \text{H}_2(g) + \text{S}_2(g)$ @ 800°C , $K_c = 1.67 \times 10^{-7}$. If a 0.500 L flask initially containing $1.25 \times 10^{-4} \text{ mol H}_2\text{S}$ is heated to 800°C , find the equilibrium concentrations.

Construct an ICE table for the reaction

determine the direction the reaction is proceeding

	$[\text{H}_2\text{S}]$	$[\text{H}_2]$	$[\text{S}_2]$
initial	$2.50\text{E}-4$	0	0
change			
equilibrium			

no products initially, $Q_c = 0$, and the reaction is proceeding f

For the reaction $2 \text{H}_2\text{S}(g) \rightleftharpoons 2 \text{H}_2(g) + \text{S}_2(g)$ @ 800°C , $K_c = 1.67 \times 10^{-7}$. If a 0.500 L flask initially containing 1.25×10^{-4} mol H_2S is heated to 800°C , find the equilibrium concentrations.

represent the change in the partial pressures in terms of x

sum the columns to find the equilibrium concentrations in terms of x

substitute into the equilibrium constant

	$[\text{H}_2\text{S}]$	$[\text{H}_2]$	$[\text{S}_2]$
initial	$2.50\text{E-}4$	0	0
change	$-2x$	$+2x$	$+x$
equilibrium	$2.50\text{E-}4 - 2x$	$2x$	x

$$K_c = \frac{[\text{H}_2]^2 [\text{S}_2]}{[\text{H}_2\text{S}]^2} = \frac{(2x)^2 (x)}{(2.50 \times 10^{-4} - 2x)^2}$$

For the reaction $2 \text{H}_2\text{S}(g) \rightleftharpoons 2 \text{H}_2(g) + \text{S}_2(g)$ @ 800°C , $K_c = 1.67 \times 10^{-7}$. If a 0.500 L flask initially containing 1.25×10^{-4} mol H_2S is heated to 800°C , find the equilibrium

since K_c is very small, approximate the $[\text{H}_2\text{S}]_{\text{eq}} = [\text{H}_2\text{S}]_{\text{init}}$ and solve for x

concentrations	$[\text{H}_2\text{S}]$	$[\text{H}_2]$	$[\text{S}_2]$
initial	$2.50\text{E-}4$	0	0
change	$-2x$	$+2x$	$+x$
equilibr	$2.50\text{E-}4 - 2x$	$2x$	x

$$K_c = \frac{[\text{H}_2]^2[\text{S}_2]}{[\text{H}_2\text{S}]^2} = \frac{(2x)^2(x)}{(2.50 \times 10^{-4} - 2x)^2} = \frac{1.67 \times 10^{-7}}{6.25 \times 10^{-8}} = \frac{4x^3}{6.25 \times 10^{-8}}$$

$$K_c = \frac{[\text{H}_2]^2[\text{S}_2]}{[\text{H}_2\text{S}]^2} = \frac{(2x)^2(x)}{(2.50 \times 10^{-4})^2}$$

$$x = \sqrt[3]{\frac{(1.67 \times 10^{-7})(6.25 \times 10^{-8})}{4}}$$

$$x = 1.38 \times 10^{-5}$$

For the reaction $2 \text{H}_2\text{S}(g) \rightleftharpoons 2 \text{H}_2(g) + \text{S}_2(g)$ @ 800°C , $K_c = 1.67 \times 10^{-7}$. If a 0.500 L flask initially containing $1.25 \times 10^{-4} \text{ mol H}_2\text{S}$ is heated to 800°C , find the equilibrium

check if the approximation is valid by seeing if $x < 5\%$ of $[\text{H}_2\text{S}]_{\text{init}}$

	$[\text{H}_2\text{S}]$	$[\text{H}_2]$	$[\text{S}_2]$
initial	$2.50\text{E-}4$	0	0
change	$-2x$	$+2x$	$+x$
equilibrium	$2.50\text{E-}4$	$2x$	x

$$\frac{1.38 \times 10^{-5}}{2.50 \times 10^{-4}} \times 100\% = 5.52\% > 5\%$$

the approximation is not valid!!

For the reaction $2 \text{H}_2\text{S}(g) \rightleftharpoons 2 \text{H}_2(g) + \text{S}_2(g)$ @ 800°C , $K_c = 1.67 \times 10^{-7}$. If a 0.500 L flask initially containing 1.25×10^{-4} mol H_2S is heated to 800°C , find the equilibrium

if approximation is
invalid, substitute
 x_{current} into K_c where
it is subtracted and
re-solve for x_{new}

$$X_{\text{current}} = 1.38 \times 10^{-5}$$

concentration	$[\text{H}_2\text{S}]$	$[\text{H}_2]$	$[\text{S}_2]$
initial	$2.50\text{E-}4$	0	0
change	$-2x$	$+2x$	$+x$
equilibrium	$2.50\text{E-}4 - 2x$	$2x$	x

$$K_c K_c = \frac{[H_2]^2 [S_2]}{(H_2S)^2} = \frac{(2x)^2 (2x)^2}{(4.58 \times 10^{-4})^2} = 3 \sqrt{\frac{(1.67 \times 10^{-7})(2.22 \times 10^{-4})^2}{4}}$$

$$1.67 \times 10^7 = \frac{4x^3}{(2.22 \times 10^4)^2} \quad x = 1.27 \times 10^5$$

For the reaction $2 \text{H}_2\text{S}(g) \rightleftharpoons 2 \text{H}_2(g) + \text{S}_2(g)$ @ 800°C , $K_c = 1.67 \times 10^{-7}$. If a 0.500 L flask initially containing $1.25 \times 10^{-4} \text{ mol H}_2\text{S}$ is heated to 800°C , find the equilibrium concentrations.

Substitute x_{current} into K_c where it is subtracted and re-solve for x_{new} . If x_{new} is the same number, you have arrived at the best approximation $x_{\text{current}} = 1.27 \times 10^{-5}$		$[\text{H}_2\text{S}]$	$[\text{H}_2]$	$[\text{S}_2]$
	initial	$2.50\text{E}-4$	0	0
	change	$-2x$	$+2x$	$+x$
	equilibrium	$2.50\text{E}-4 - 2x$	$2x$	x

$$K_c = \frac{[\text{H}_2]^2 [\text{S}_2]}{[\text{H}_2\text{S}]^2} = \frac{(2x)^2 (x)}{(2.50 \times 10^{-4} - 2x)^2} = 1.67 \times 10^{-7}$$

$$x^3 = \frac{(1.67 \times 10^{-7})(2.25 \times 10^{-4})^2}{4}$$

$$1.67 \times 10^{-7} = \frac{4x^3}{(2.25 \times 10^{-4})^2}$$

$$x = 1.28 \times 10^{-5}$$

since $x_{\text{current}} = x_{\text{new}}$, approx. OK

For the reaction $2 \text{H}_2\text{S}(g) \rightleftharpoons 2 \text{H}_2(g) + \text{S}_2(g)$ @ 800°C , $K_c = 1.67 \times 10^{-7}$. If a 0.500 L flask initially containing 1.25×10^{-4} mol H_2S is heated to 800°C , find the equilibrium

substitute x_{current}
into the
equilibrium
concentration
definitions and
solve

	$[\text{H}_2\text{S}]$	$[\text{H}_2]$	$[\text{S}_2]$
initial	$2.50\text{E-}4$	0	0
change	$-2x$	$+2x$	$+x$
equilibrium	$2.50\text{E-}4 - 2x$	$2.56\text{E-}5$	$1.28\text{E-}5$
	$x_{\text{current}} = 1.28 \times 10^{-5}$		

$$[\text{H}_2\text{S}] = 2.50 \times 10^{-4} - 2x = 2.50 \times 10^{-4} - 2(1.28 \times 10^{-5}) = 2.24 \times 10^{-4} \text{ M}$$

$$[\text{H}_2] = 2x = 2(1.28 \times 10^{-5}) = 2.56 \times 10^{-5} \text{ M}$$

$$[\text{S}_2] = x = 1.28 \times 10^{-5} \text{ M}$$

For the reaction $2 \text{H}_2\text{S}(g) \rightleftharpoons 2 \text{H}_2(g) + \text{S}_2(g)$ @ 800°C , $K_c = 1.67 \times 10^{-7}$. If a 0.500 L flask initially containing 1.25×10^{-4} mol H_2S is heated to 800°C , find the equilibrium

check by substituting the equilibrium concentrations back into the equilibrium constant expression and comparing the calculated K_c to the given K_c

concentrations	$[\text{H}_2\text{S}]$	$[\text{H}_2]$	$[\text{S}_2]$
initial	$2.50\text{E}-4$	0	0
change	$-2x$	$+2x$	$+x$
equilibrium	$2.24\text{E}-4$	$2.56\text{E}-5$	$1.28\text{E}-5$

$$K_c = \frac{[\text{H}_2]^2 [\text{S}_2]}{[\text{H}_2\text{S}]^2} = \frac{(2.56 \times 10^{-5})^2 (1.28 \times 10^{-5})}{(2.24 \times 10^{-4})^2} = 1.67 \times 10^{-7}$$

$K_c(\text{calculated}) = K_c(\text{given})$ within significant figures

**For the reaction $\text{I}_2(g) \rightleftharpoons 2 \text{I}(g)$
where $K_c = 3.76 \times 10^{-5}$ at 1000 K.**

**If 1.00 mol of I_2 is placed into a
2.00L flask and heated, what will
be the equilibrium
concentrations of $[\text{I}_2]$ and $[\text{I}]$?**

**(Recall that we solved this
problem using the quadratic
equation, now use the
simplifying assumption that K is
small and x is small to solve for**

x)

For the reaction $\text{I}_2(g) \rightleftharpoons 2 \text{I}(g)$ the value of

$K_c = 3.76 \times 10^{-5}$ at 1000 K. If 1.00 moles of I_2 is placed into a 2.00 L flask and

heated, what will be the equilibrium concentrations of $[\text{I}_2]$ and $[\text{I}]$?	$[\text{I}_2]$	$[\text{I}]$
initial	0.500	0
change	$-x$	$+2x$
equilibrium	$0.500 - x$	$2x$

Since $[\text{I}]_{\text{initial}} = 0$, $Q = 0$ and the reaction must proceed forward

$$K_c = \frac{[\text{I}]^2}{[\text{I}_2]}$$

$$3.76 \times 10^{-5} = \frac{(2x)^2}{(0.500 - x)} = \frac{(2x)^2}{0.500}$$

$$3.76 \times 10^{-5}(0.500) = 4x^2$$

For the reaction $\text{I}_2(g) \rightleftharpoons 2 \text{I}(g)$ the value of

$K_c = 3.76 \times 10^{-5}$ at 1000 K. If 1.00 moles of I_2 is placed into a 2.00 L flask and

heated, what will be the equilibrium

concentrations of $[\text{I}_2]$ and $[\text{I}]$?

	$[\text{I}_2]$	$[\text{I}]$
initial	0.500	0
change	$-x$	$+2x$
equilibrium	$0.500 - x$	$2x$

$$3.76 \times 10^{-5} = \frac{(2x)^2}{0.500 - x}$$

$$1.88 \times 10^{-5} = 4x^2$$

$$\frac{2.17 \times 10^{-3}}{0.500} \times 100\% = 0.434\% < 5\%$$

$$\sqrt{\frac{1.88 \times 10^{-5}}{4}} = x = 2.17 \times 10^{-3}$$

the approximation is valid!!

For the reaction $\text{I}_2(g) \rightleftharpoons 2 \text{I}(g)$ the value of

$K_c = 3.76 \times 10^{-5}$ at 1000 K. If 1.00 moles of I_2 is placed into a 2.00 L flask and

heated, what will be the equilibrium concentrations of I_2 and I ?

	$[\text{I}_2]$	$[\text{I}]$
initial	0.500	0
change	$-x$	$+2x$
equilibrium	$0.500 - x$	$2x$

$$x = 0.00217$$

$$0.500 - 0.00217 = 0.498$$

$$[\text{I}_2] = 0.498 \text{ M}$$

$$2(0.00217) = 0.00434$$

$$[\text{I}] = 0.00434 \text{ M}$$

$$\sqrt{K_c} = \frac{[\text{I}]}{[\text{I}_2]} = \frac{(0.00434)}{(0.498)} = 3.78 \times 10^{-5} \quad \square$$

Disturbing and Re-establishing

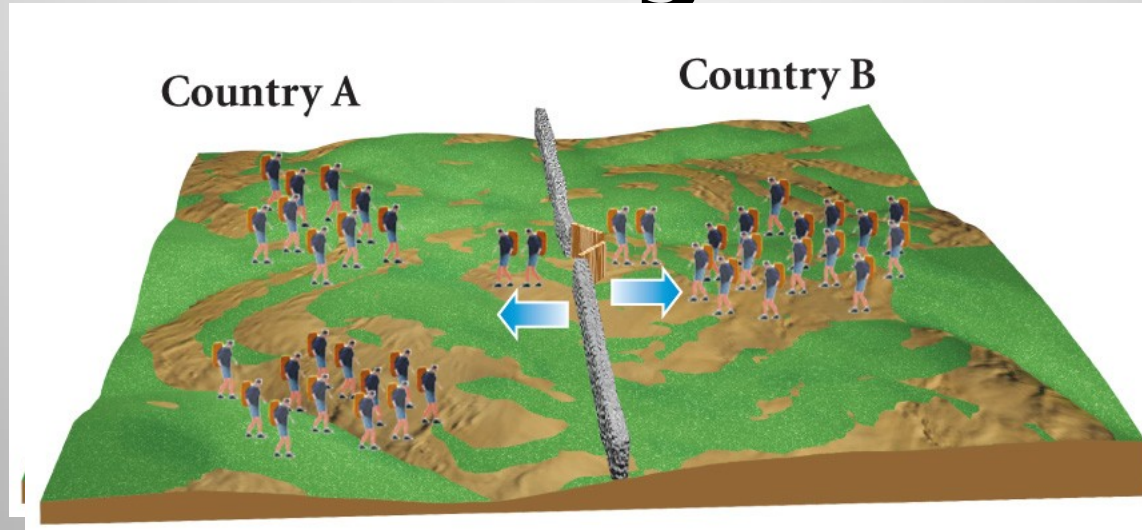
Equilibrium

- once a reaction is at equilibrium, the concentrations of all the reactants and products remain the same
- however if the conditions are changed, the concentrations of all the chemicals will change until equilibrium is re-established
- the new concentrations will be different, but the equilibrium constant will be the same
 - unless you change the temperature

Le Châtelier's Principle

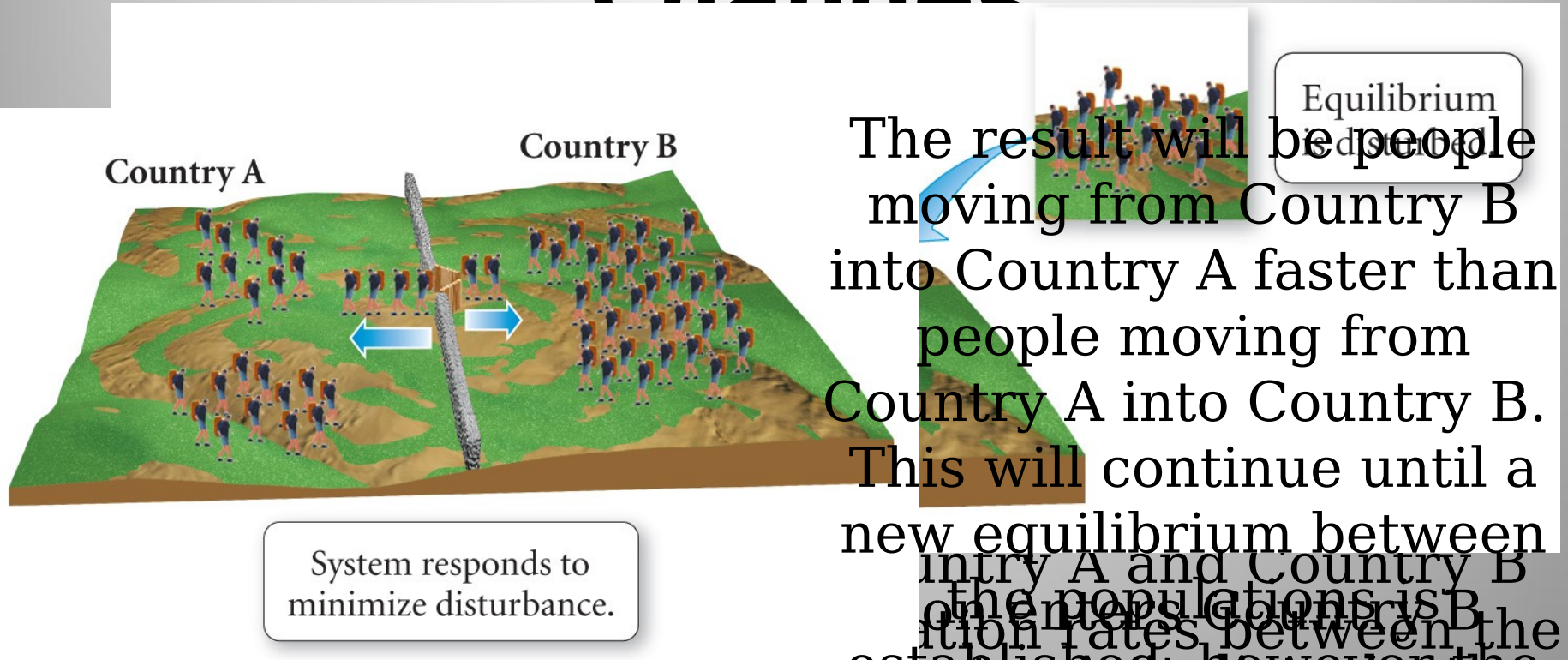
- Le Châtelier's Principle guides us in predicting the effect various changes in conditions have on the position of equilibrium
- it says that if a system at equilibrium is disturbed, the position of equilibrium will shift to minimize the disturbance
 - disturbances all involve making the system open

An Analogy: Population Changes



However, as time passes, when Country A citizens feel overcrowded, some will emigrate to Country B. Similarly, when Country B citizens feel overcrowded, some will emigrate to Country A. This process will occur in both directions at the same rate, leading to populations in Country A and Country B that are constant, though not necessarily equal.

An Analogy: Population Changes



The result will be people moving from Country B into Country A faster than people moving from Country A into Country B. This will continue until a new equilibrium between Country A and Country B is established. However, the population rates between the two states are equal so the populations stay constant. From somewhere outside, new populations will have different numbers of people than the old ones.

The Effect of Concentration Changes on Equilibrium

- Adding a reactant will decrease the amounts of the other reactants and increase the amount of the products until a new position of equilibrium is found
 - that has the same K
- Removing a product will increase the amounts of the other products and decrease the amounts of the reactants.
 - you can use this to drive a reaction to completion!
- **Equilibrium shifts away from side with added chemicals or toward side with removed chemicals**
- Remember, adding more of a solid or liquid does not change its concentration – and therefore has no effect on the equilibrium

Disturbing Equilibrium: Adding or Removing Reactants

- after equilibrium is established,
 - how will adding a reactant affect the rate of the forward reaction?
 - how will it affect the rate of the reverse reaction?
 - what will this cause?
 - how will it affect the value of K ?
 - how will removing a reactant affect the rate of the forward reaction?
 - How will it affect the rate of the reverse reaction? What will this cause?
 - How will it affect the value of K ?
- as long as the added reactant is included in the equilibrium constant expression
i.e., not a solid or liquid

Disturbing Equilibrium: Adding Reactants

- adding a reactant initially
 - increases the rate of the forward reaction, but has no initial effect on the rate of the reverse reaction.
 - the reaction proceeds to the right until equilibrium is re-established.
- at the new equilibrium position, you will have
 - more of the products than before,
 - less of the non-added reactants than before,
 - less of the added reactant
- at the new equilibrium position, the concentrations of reactants and products will be such that the value of the equilibrium constant is the same

Disturbing Equilibrium: Removing Reactants

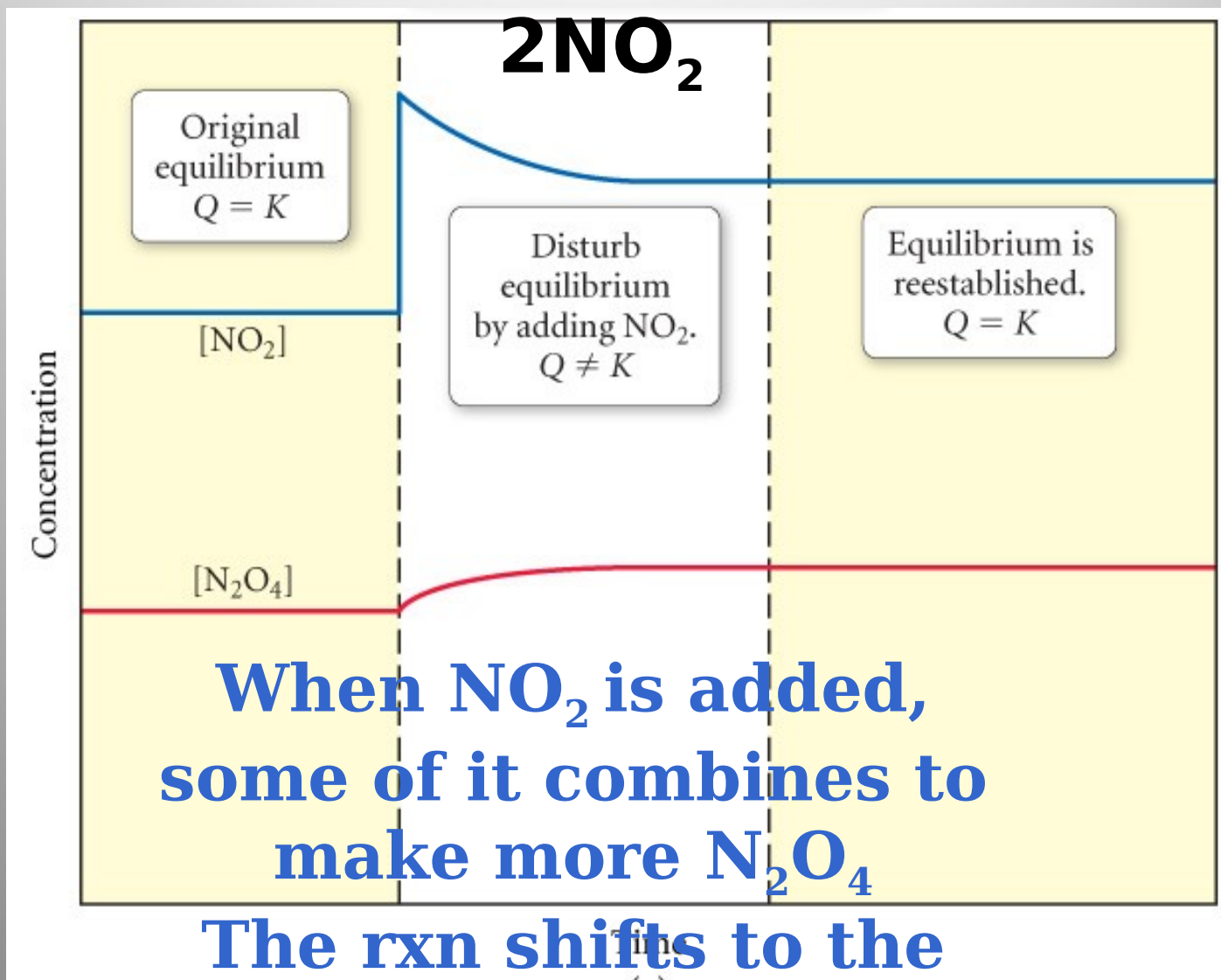
removing a reactant initially decreases the rate of the forward reaction, but has no initial effect on the rate of the reverse reaction.

- so the reaction is going faster in reverse
- the reaction proceeds to the left until equilibrium is re-established.
- at the new equilibrium position, you will have less of the products than before, more of the non-removed reactants than before, and more of the removed reactant
 - but not as much of the removed reactant as you had before the removal
- at the new equilibrium position, the concentrations of reactants and products will be such that the value of the equilibrium constant is the same

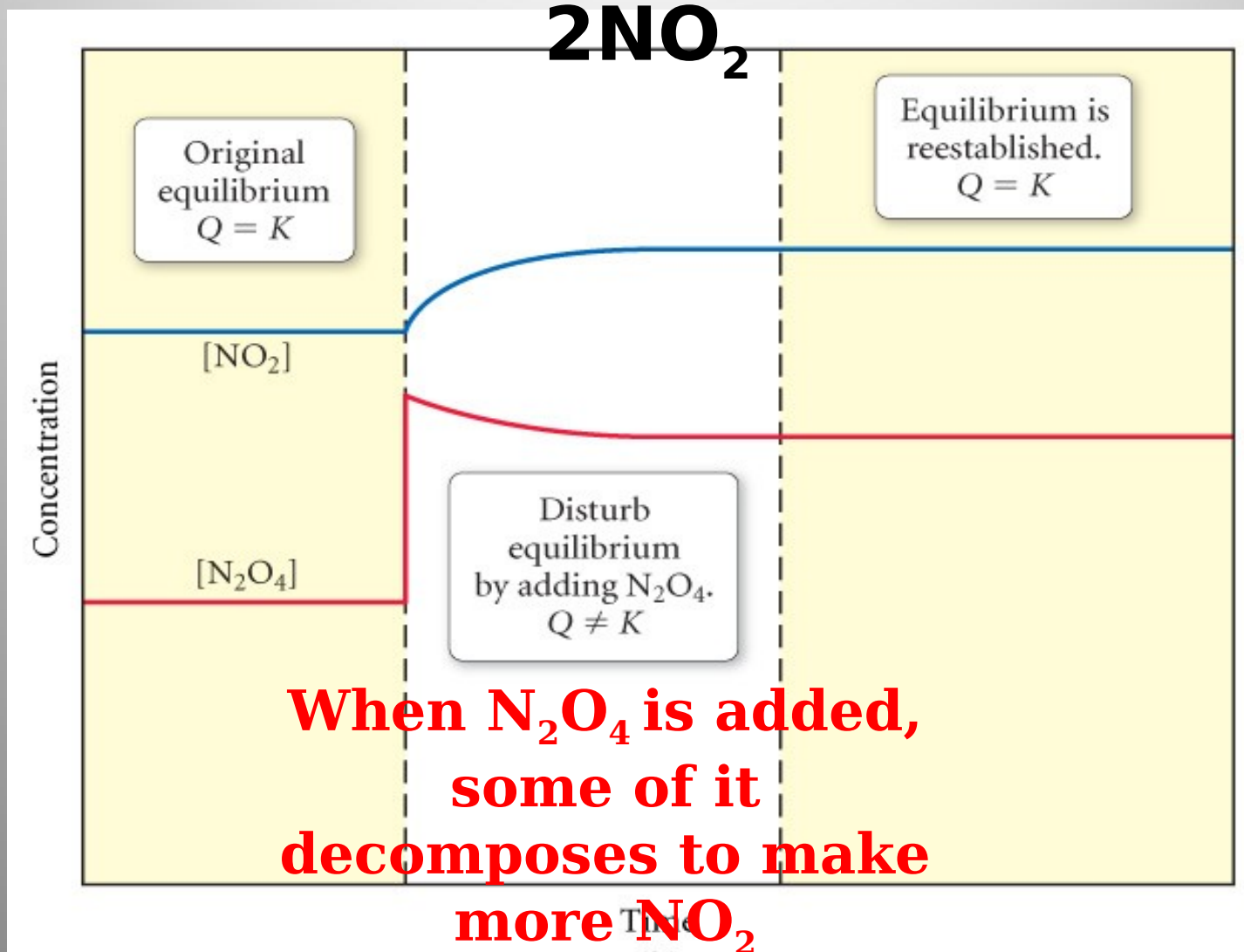
The Effect of Adding a Gas to a Gas Phase Reaction at Equilibrium

- adding a gaseous reactant increases its partial pressure, causing the equilibrium to the right
 - increasing its partial pressure increases its concentration
 - does not increase the partial pressure of the other gases in the mixture
- adding an inert gas to the mixture has no effect on the position of equilibrium
 - does not effect the partial pressures of the gases in the reaction

The Effect of Concentration Changes on Equilibrium: $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$



The Effect of Concentration Changes on Equilibrium: $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$



**When N_2O_4 is added,
some of it
decomposes to make
more NO_2**

The rxn shifts to the

*****Disturbing Equilibrium: Changing the Volume**

- after equilibrium is established,
 - How will decreasing the container volume affect the total pressure of solids, liquid, and gases?
 - How will it affect the concentration of solids, liquid, solutions, and gases?
 - What will this cause?
 - How will it affect the value of K ?

Effect of Volume Change on Equilibrium

- Decreasing volume \longrightarrow increases total pressure
 - Boyle's Law
 - total pressure increases \longrightarrow partial pressures increase
 - Dalton's Law of Partial Pressures
- Decreasing volume \longrightarrow increases concentration
 - # moles constant, # liters decreases, resulting in higher molarity
- according to Le Châtelier's Principle, the equilibrium should shift to mitigate that pressure increase

Disturbing Equilibrium:

Reducing Volume

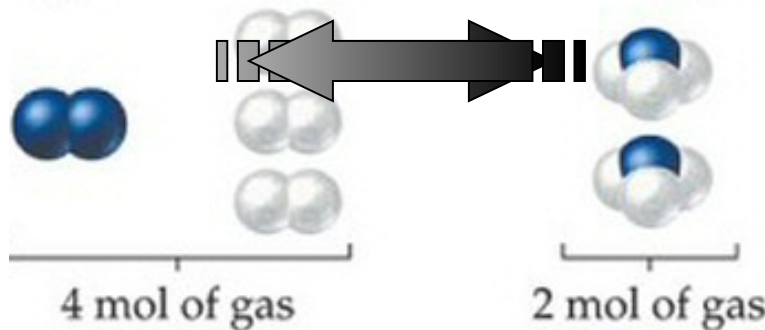
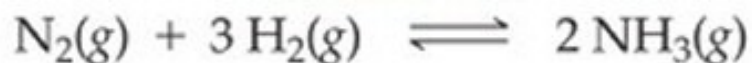
- the way the system reduces the pressure is to reduce the number of gas molecules in the container
- **when the volume decreases, the equilibrium shifts to the side with fewer gas molecules**
- at the new equilibrium position
 - the partial pressures of gaseous reactants and products will be at a new value
 - the equilibrium constant will be the same as before

Disturbing Equilibrium:

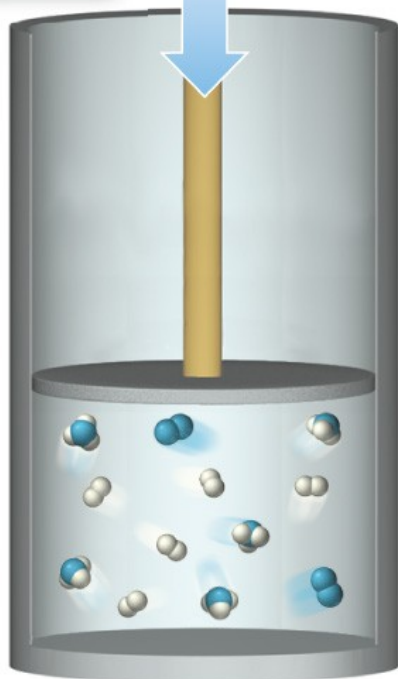
Reducing Volume

- for solids, liquids, or solutions, changing the size of the container has no effect on the concentration, therefore no effect on the position of equilibrium

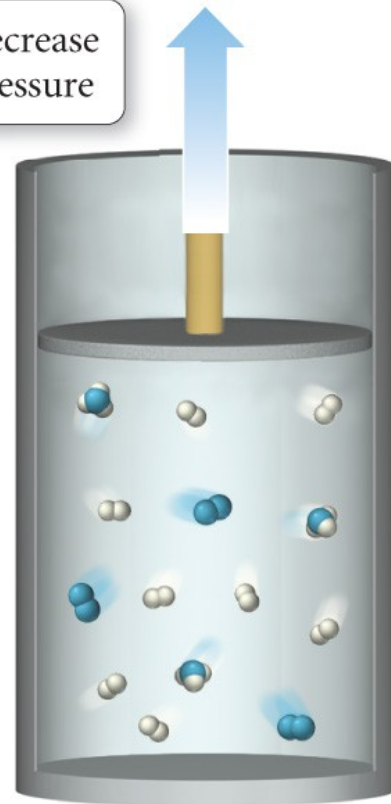
The Effect of Volume Changes on Equilibrium



Increase
pressure



Decrease
pressure



When the pressure is decreased by increasing the volume, the position of equilibrium shifts toward the side with the greater number of molecules. The system is resistant to change.

The Effect of Temperature Changes on Equilibrium Position

- exothermic reactions release energy
- endothermic reactions absorb energy
- if we write Heat as a product in an exothermic reaction or as a reactant in an endothermic reaction, it will help us use Le Châtelier's Principle to predict the effect of temperature changes
 - even though heat is not matter and not written in a proper equation

The Effect of Temperature Changes on Equilibrium for Exothermic Reactions

- for an exothermic reaction, heat is a product
- increasing the temperature is like adding heat
- according to Le Châtelier's Principle, the equilibrium will shift away from the added heat

The Effect of Temperature Changes on Equilibrium for Exothermic Reactions

- adding heat to an exothermic reaction will shift the reaction toward reactants (to the left)
 - It would decrease the concentrations of products and increase the concentrations of reactants



- adding heat to an exothermic reaction will decrease the value of K

$$\begin{array}{ccc} \downarrow & K_c = \frac{[C]^c \times [D]^d}{[A]^a \times [B]^b} & \downarrow \uparrow \end{array}$$

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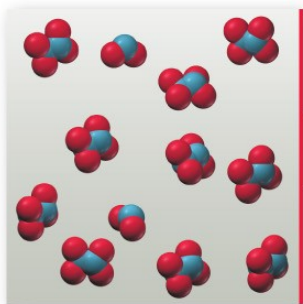
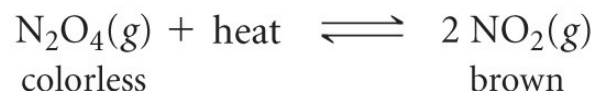


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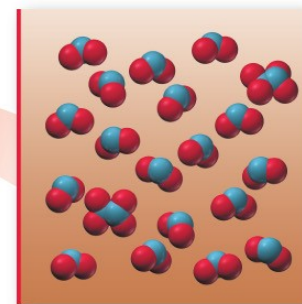
$$K_c = \frac{[C]^c \times [D]^d}{[A]^a \times [B]^b}$$

The Effect of Temperature Changes on Equilibrium

Le Châtelier's Principle: Changing Temperature



Lower temperature:
 N_2O_4 favored

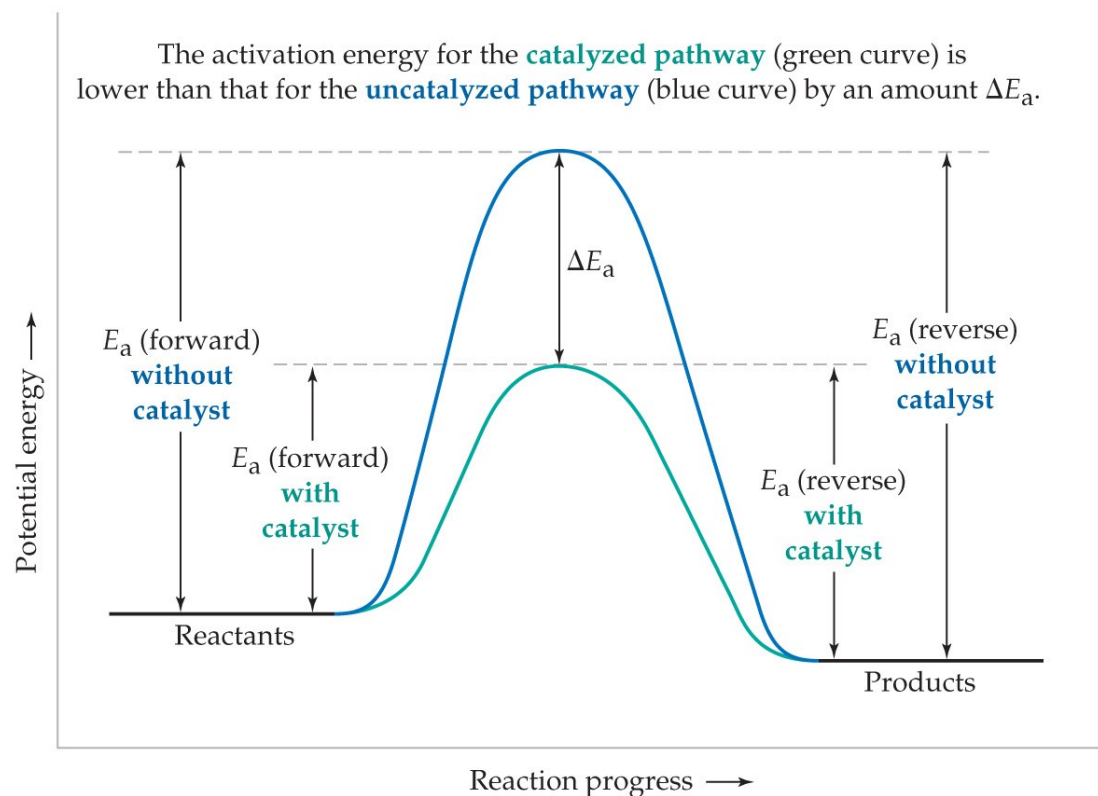


Higher temperature:
 NO_2 favored

Not Changing the Position of Equilibrium - Catalysts

- catalysts provide an alternative, more efficient mechanism
- works for both forward and reverse reactions
- affects the rate of the forward and reverse reactions by the same factor
- therefore **catalysts do not affect the position of equilibrium**

The Effect of a Catalyst on Equilibrium



Because the forward and reverse reactions pass through the same transition state, the catalyst lowers the activation energy barrier for the forward and reverse reactions by the same amount. The catalyst therefore accelerates the forward and reverse reactions by the same factor, and the composition of the equilibrium mixture is unchanged.

Practice - Le Châtelier's

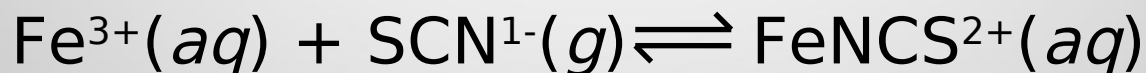
Principle

- The reaction $2 \text{SO}_2(g) + \text{O}_2(g) \rightleftharpoons 2 \text{SO}_3(g)$ with $\Delta H^\circ = -198 \text{ kJ}$ is at equilibrium. How will each of the following changes affect the equilibrium concentrations of each gas once equilibrium is re-established?
 - adding more O_2 to the container
 - condensing and removing SO_3
 - compressing the gases
 - cooling the container
 - doubling the volume of the container
 - warming the mixture
 - adding the inert gas helium to the container
 - adding a catalyst to the mixture

Practice - Le Châtelier's Principle

- The reaction $2 \text{SO}_2(g) + \text{O}_2(g) \rightleftharpoons 2 \text{SO}_3(g)$ with $\Delta H^\circ = -198 \text{ kJ}$ is at equilibrium. How will each of the following changes affect the equilibrium concentrations of each gas once equilibrium is re-established?
 - adding more O_2 to the container shift to SO_3
 - condensing and removing SO_3 shift to SO_3
 - compressing the gases shift to SO_3
 - cooling the container shift to SO_3
 - doubling the volume of the container shift to SO_2
 - warming the mixture shift to SO_2
 - adding helium to the container no effect
 - adding a catalyst to the mixture no effect

Altering an Equilibrium Mixture: Concentration



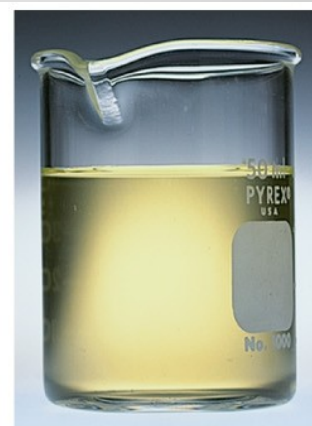
(a) Original solution: Fe^{3+} (pale yellow), SCN^{-} (colorless), and FeNCS^{2+} (red).



(b) After adding FeCl_3 to (a): $[\text{FeNCS}^{2+}]$ increases.



(c) After adding KSCN to (a): $[\text{FeNCS}^{2+}]$ increases.



(d) After adding $\text{H}_2\text{C}_2\text{O}_4$ to (a): $[\text{FeNCS}^{2+}]$ decreases as $[\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}]$ increases.



(e) After adding HgCl_2 to (a): $[\text{FeNCS}^{2+}]$ decreases as $[\text{Hg}(\text{SCN})_4^{2-}]$ increases.

STOP